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Uncatalyzed synthesis, thermal and mechanical properties of polyurethanes based on poly(ϵ -caprolactone) and 1,4-butane diisocyanate with uniform hard segment

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Abstract

Polyurethanes based on poly(ϵ -caprolactone) (PCL) (750–2800 g/mol) and 1,4-butane diisocyanate (BDI) with different soft segment lengths and constant uniform hard segment length were synthesized in absence of catalysts for the production of a degradable meniscus scaffold. First the polyesterdiols were endcapped with BDI yielding a macrodiisocyanate with a minimal amount of side reactions and a functionality of 2.0. Subsequently, the macrodiisocyanates were extended with 1,4-butanediol in order to obtain the corresponding polyurethane. The polyurethanes had molecular weights between 78 and 160 kg/mol.

Above molar masses of 1900 g/mol of the polyesterdiol crystalline PCL was found while the hard segment showed an increase in melting point from 78 to 122 °C with increasing hard segment content. It was estimated that the percentage crystallinity of the hard segment varied between 92 and 26%. The Young's modulus varied between 30 and 264 MPa, the strain at break varied between 870 and 1200% and tear strengths varied between 97 and 237 kJ/m².

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Keywords: Polyurethane; Degradation; Polycaprolactone; Elastomer; Scaffold

1. Introduction

In the past a broad range of materials has been used for degradable meniscus scaffolds although these materials all showed several disadvantages like lack of mechanical properties, biocompatibility or the impossibility to produce a suitable scaffold from the material [1–7]. A potentially suitable material might be found in the category of polyurethanes since they are known to be biocompatible while a broad range of properties can be obtained with this type of copolymer.

Generally, polyurethanes are made by reacting a polyol with a diisocyanate followed by chain extension with a diol. Commonly used polyurethanes are based on aromatic diisocyanates. These, however, lack biocompatibility due to toxic degradation products originating from the aromatic hard segment [8–12]. Hard segments based on 1,4-butane diisocyanate (BDI) can be a good non-toxic alternative since the degradation products are expected to be 1,4-butanedi-amine, putrescine, a non-toxic diamine that is, among other functions, essential for cell growth and differentiation [13–15].

In the past it has been shown that polyurethanes with a hard segment based on BDI can possess suitable mechanical properties [16–19]. It has also been shown

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that polyurethaneureas based on BDI have a tear strength that is sufficient to prevent rupture of the sutures out of the meniscus scaffold during the implantation [17,20], although these polymers were difficult to process into scaffolds.

An important requirement for a suitable meniscus reconstruction material is that the scaffold should degrade relatively slowly without swelling during degradation [21]. It is anticipated that a period of at least a year is required for the meniscus to regenerate and being able to take over the mechanical load from the scaffold. Poly(ϵ -caprolactone) is commonly used as soft segment in polyurethanes [22], known to be biocompatible, slowly hydrolytically and enzymatically degradable and already used for several long term applications [23] and is expected to be very suitable as meniscus reconstruction material. Usually, these syntheses are carried out with the aid of a catalyst, but catalysts do not only catalyze chain extensions but also promote several side reactions [24]. Moreover, the absence of catalysts will also increase biocompatibility [25,26].

In this work the catalyst-free synthesis of polyurethanes with a uniform hard segment based on 1,4-BDI, 1,4-butanediol and poly(ϵ -caprolactone) as soft segment is described. The thermal and mechanical properties are evaluated as a function of the soft segment length.

2. Experimental

2.1. Materials

1,4-Butanediol (BDO, Aldrich) was distilled from 3 Å molecular sieves. 1,4-Butane diisocyanate (BDI, Bayer) and ϵ -caprolactone (Union Carbide) (from CaH_2) were distilled under reduced pressure. Dioxane (Merck) and *n*-butanol (Merck) were distilled from sodium, hexane (Merck) from LiAlH_4 . Before use the Petri dishes were siliconized with a silicone solution from SERVA (Heidelberg, Germany).

2.2. Equipment

^1H -NMR spectra were recorded at room temperature using a 300 MHz Varian NMR apparatus. A Perkin-Elmer DSC-7 was used for thermal analysis and was operated under a nitrogen atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$.

DMTA measurements were conducted using a Rheometrics solids analyzer RSA II at a frequency of 1 Hz with a heating rate of $2^\circ\text{C}/\text{min}$.

Molecular weights of the polyurethanes were determined by GPC measurements using dimethylformamide with 0.01 M LiBr as eluent on a Waters 600 Powerline system using conventional calibration with polystyrene standards. GPC measurements of the polyols were performed with THF. Intrinsic viscosities of the polymers in chloroform at 25°C were determined using a type Oa Ubbelohde viscometer.

Infrared Spectroscopy (FT-IR) was done using a Mattson Instruments 'Galaxy' equipped with a Golden Gate single reflection ATR accessory.

Tensile tests were performed using rectangular ($40 \times 2.2 \times 0.1$ mm) shaped specimens and an extension rate of 10 mm/min using an Instron (4301) tensile tester. The yield points were determined according to ASTM E111. The tear strength was determined according to ASTM D1938-62T.

2.3. Synthesis of the poly(ϵ -caprolactone) polyester, a typical procedure

A mixture of ϵ -caprolactone (29.10 g; 0.255 mol) and the initiator BDO (1.74 g; 0.019 mol) were reacted at 150°C for 7 days under an argon atmosphere to yield a polyester having a molecular weight of 1600 g/mol. ^1H -NMR spectroscopy was used to verify the complete conversion of the polymerization. Six different poly(ϵ -caprolactone) diols were synthesized: 750, 1000, 1600, 1900, 2200 and 2800 g/mol. The reaction is depicted in Fig. 1.

^1H -NMR (CDCl_3 , δ 7.26): δ 4.10 (d, 2H; OCH_2), 3.65 (t; HOCH_2), 2.25 (t, 2H; CH_2CO), 1.62 (q, 2H; $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.40 (q, 2H; $\text{OCH}_2\text{CH}_2\text{CH}_2$).

FT-IR (ATR): 3533, 2945, 2866, 1721, 1160 cm^{-1} .

2.4. Isocyanate terminated poly(ϵ -caprolactone) polyester, a typical procedure

A mixture of poly(ϵ -caprolactone) diol (28.07 g; 17.5 mmol) and a six-fold excess of BDI (29.5 g; 0.21 mol) were reacted at 80°C for 4 h under an argon atmosphere. The excess of BDI was removed using a short path distillation apparatus operating at 80°C and 1×10^{-2} mbar. Distillation was performed until a

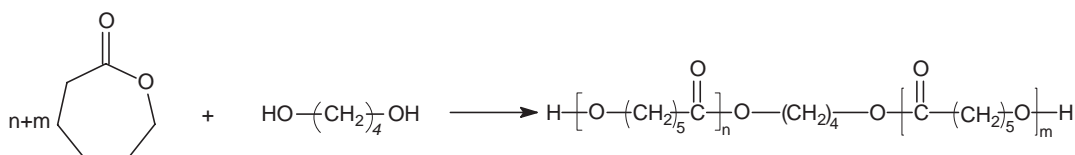
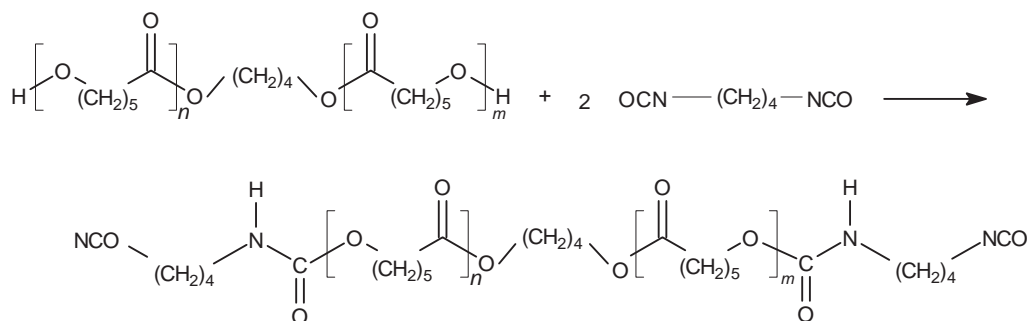
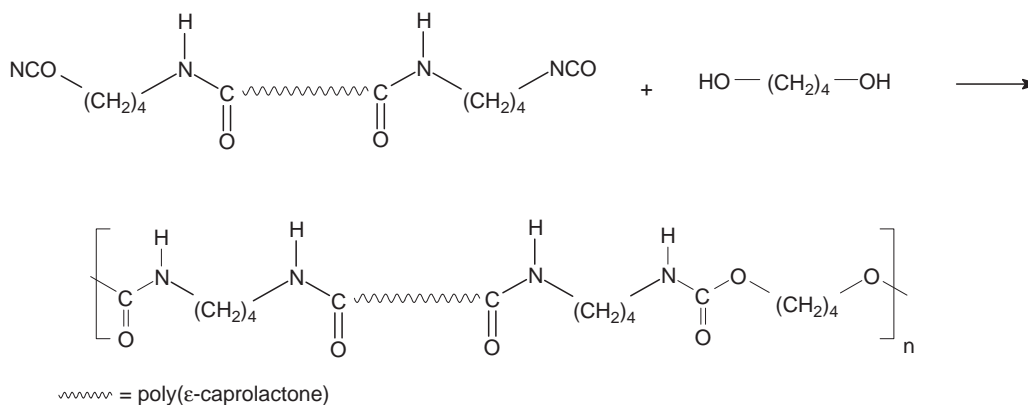
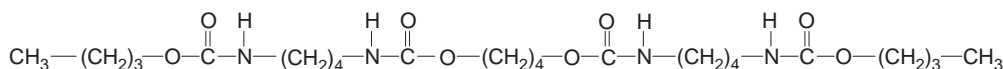


Fig. 1. Polymerization of the poly(ϵ -caprolactone) polyester.

Fig. 2. Endcapping of the poly(ϵ -caprolactone) polyester with 1,4-BDI.Fig. 3. Chain extension reaction of the endcapped poly(ϵ -caprolactone) with 1,4-butanediol.Fig. 4. The pure hard segment terminated with *n*-butanol.

constant weight was reached (about 24 h). The reaction is depicted in Fig. 2.

$^1\text{H-NMR}$ (CDCl_3 δ 7.26): δ 4.85 (t; CH_2NHCO), 4.05 (d, 2H; OCH_2), 3.30 (t; OCNCH_2), 3.10 (q; CH_2NH), 2.30 (t; CH_2CO), 1.80 (q; $\text{OCNCH}_2\text{CH}_2\text{CH}_2$), 1.62 (q; $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.30 (q, 2H; $\text{OCH}_2\text{CH}_2\text{CH}_2$).

FT-IR (ATR): 3334, 2942, 2864, 2261, 1791, 1532, 1470, 1363, 1237, 1164, 1106, 1043, 959, 730.

2.5. Chain extension of the isocyanate terminated poly(ϵ -caprolactone) polyester, a typical procedure

The isocyanate terminated polyester (30.23 g; 16.1 mmol) was reacted with a slight excess of BDO (1.48 g; 16.4 mmol) for 72 h at 80 °C under argon atmosphere. Depending on the molecular weight of the polyester the mixture turned opaque after a few hours. PU1600-100 °C was extended at 100 °C for 16 h and PU2800-60 °C was extended at 60 °C for 72 h. The reaction is depicted in Fig. 3.

$^1\text{H-NMR}$ (CDCl_3 δ 7.26): δ 4.85 (t; CH_2NHCO), 4.05 (d; OCH_2), 3.10 (q; CH_2NH), 2.30 (t; CH_2CO), 1.62 (q; $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.45 (q; OCH_2CH_2), 1.30 (q; $\text{OCH}_2\text{CH}_2\text{CH}_2$).

FT-IR (ATR): 3314, 2953, 2869, 1725, 1681, 1535, 1461, 1374.

2.6. Synthesis of the 1-butanol BDI–BDO–BDI adduct

A mixture of BDO (0.27 g, 3.0 mmol) and BDI (5.53 g, 39.5 mmol) were reacted at 80 °C for 4.5 h under an argon atmosphere. This was washed with distilled hexane. The product was isolated on a glass filter and dried overnight under vacuum. Subsequently the formed BDI–BDO–BDI (0.25 g, 0.675 mmol) was reacted with a 6.5-fold excess of *n*-butanol (2 ml, 21.9 mmol) at 80 °C for 4.5 h under an argon atmosphere. This was washed with distilled hexane. The product was isolated on a glass filter and dried overnight under vacuum (Fig. 4).

$^1\text{H-NMR}$ (CDCl_3 δ 7.26): δ 4.70 (t, 1H; CH_2NHCO), 4.10, 3.10 (q, 2H; CH_2NH), 1.62 (q, 2H;

OCH₂CH₂CH₂), 1.50, 1.30, 1.20 (m, 2H; CH₂CH₃), 0.90 (t, 3H; CH₂CH₃).

2.7. Film casting

The polymer was shredded and dissolved at 80 °C in dioxane up to a concentration of 20 g/L for 3 h. After the dissolution of the polymer the solution was poured into a Petri dish. The solvent was evaporated at 60 °C in 3 h. To complete the drying the films were placed in a vacuum oven at 50 °C for 24 h.

3. Results and discussion

3.1. Synthesis

3.1.1. poly(ϵ -caprolactone) (PCL)

PCL was synthesized by reacting the initiator, BDO with ϵ -caprolactone in different ratios. The molecular weight of the different PCL polyols was estimated with the ratio between HO-CH₂ (3.6 ppm) and COOCH₂ (4.0 ppm) obtained with ¹H-NMR. As can be seen in Table 1 the different molecular weights measured with NMR and GPC for the PCL polyols correspond very well to the ratio of monomer to initiator used.

The polydispersity of the polyols can have a major influence on the phase separation of hard and soft segment. As can be seen in Table 1 the polydispersity of the polyols is low and constant with different molecular weights.

Subsequently, the PCL was endcapped using a six-fold excess of BDI to obtain an isocyanate-terminated prepolymer. In this step it is very important to prevent side reactions such as trimerization or allophanate formation. These side reactions will lead to functionalities higher than 2 resulting in branching or even crosslinking of the polyurethane. After endcapping the excess of BDI was removed and the distillation was complete when the endcapped polyol reached a constant weight. Via the amount of BDI that was needed for endcapping the molecular weight of PCL can be

calculated using Formula 1

$$M_n(\text{g/mol}) = \frac{(1/2)140.114 \text{ g/mol } W_{\text{PCL}}(\text{g})}{W_{\text{BDI}}(\text{g})}, \quad (1)$$

where M_n is the molecular weight of the PCL, W_{PCL} is the amount of PCL used for endcapping and W_{BDI} is the amount of BDI needed for endcapping. We observed that the molecular weight of PCL determined via endcapping is in very good agreement with the molecular weight calculated from the monomer/initiator ratio, which suggests a minimum amount of side reactions. Molecular weights calculated by the distillation method were used to determine the amount of BDO needed for chain extension.

3.1.2. Polyurethane

It is known that during extension an excess of isocyanate groups will lead to crosslinking and the formation of insoluble polymers [27]. For this reason a small excess of 1% chain extender, BDO, is used to compensate for the minor amount of BDO that evaporated during extension and to make sure that after chain extension the polymer will have hydroxyl endgroups instead of reactive isocyanate groups. After extension in the bulk it was found that there were still reactive isocyanate groups present (FT-IR). These last remaining isocyanate and hydroxyl groups reacted on dissolving the polymer for film casting. The obtained polyurethanes were analyzed using viscometry, GPC, FTIR and NMR (Table 2). In the cast films no isocyanate groups could be detected with ¹H-NMR and FT-IR anymore. The polymer films were completely soluble in chloroform, dioxane, toluene, dimethylsulfoxide, dimethylformamide and *N*-methyl-2-pyrrolidone.

It was found that polymers based on PCL of 1900 g/mol or shorter had a polydispersity around two whereas PU2200 and PU2800 showed values of 3.5 and higher. This is an indication that side reactions occurred during extension of PU2200 and 2800. Surprisingly, polymers containing the lowest concentration of reactive groups exhibit the most side reactions. Based on concentrations of reactive groups one would expect the opposite, an increase in concentration should give an increase in side

Table 1
Molecular weights of the polyols determined via monomer/initiator ratio, NMR, GPC and endcapping

Polymer code	M_n (M/I ratio) (g/mol)	M_n (NMR) (g/mol)	M_n (GPC) (g/mol)	D (GPC) (–)	M_n (distillation) (g/mol)
PCL750	750	790	790	1.14	760
PCL1000	1000	1090	1080	1.36	1000
PCL1600	1600	1660	1990	1.24	1570
PCL1900	1900	1950	2350	1.10	1910
PCL2200	2200	2250	2910	1.20	2200
PCL2800	2800	3200	3020	1.17	2780

(M/I ratio: monomer/initiator ratio).

Table 2
GPC and intrinsic viscosity measurements of the synthesized polyurethanes

Polymer code	Theoretical HSC (%)	Measured ^a HSC (%)	$[\eta]_{\text{bulk}}$ (dl/g)	$[\eta]_{\text{film}}$ (dl/g)	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n (–)
PU750	33.0	32.8	0.65	0.82	103.9	195.8	1.9
PU1000	27.0	26.2	n.d.	1.17	108.2	275.2	2.5
PU1600	18.8	18.2	1.12	1.81	156.1	349.2	2.2
PU1900	16.3	14.2	1.13	1.98	163.5	338.6	2.1
PU2200	14.4	14.3	1.10	2.65	155.2	542.4	3.5
PU2800	11.7	13.6	1.65	2.96	162.7	639.2	3.9
PU2800-60 °C	11.7	11.3	n.d.	1.28	78.6	155.8	2.0
PU1600-100 °C	18.8	19.2	1.20	2.31	139.5	499.9	3.6

n.d. not determined.

^aAs determined by ¹H-NMR using the 2.25 and 3.13 ppm peaks.

Table 3
DSC & DMTA results of the polyurethanes

Polymer code	T_g polyol (°C)	T_g (°C)	T_m PCL (°C)	ΔH_{PCL} (J/g)	Crystalline PCL (%)	T_m HS (°C)	ΔH_{HS} (J/g)	T_f (°C) (DMTA)
PU750	–80.1	–45.9	—	—	—	121.7	51.7	109
PU1000	–77.6	–53.0	—	—	—	109.9	38.4	105
PU1600	–73.3	–52.1	—	—	—	94.0	22.3	93
PU1900	–76.1	–57.4	4.2	2.8	2.5	87.4	15.4	86
PU2200	–70.5	–56.4	16.4	11.5	9.9	79.5	15.0	71
PU2800	–72.3	–58.5	37.7	11.4	9.5	78.0	5.2	77

—: not present.

reactions. It is not expected that side reactions occur during endcapping since endcapping conditions were the same for all polymers and would, based on concentrations, also suggest the opposite. Moreover, after 6 h of endcapping and distillation 99% of the BDI has been removed, while the extension lasts for 72 h.

As will be shown later, this series of polymers shows a decrease in melting temperature with a decrease in hard segment concentration. The polymers PU2200 and PU2800 both have a melting point near the reaction temperature of 80 °C and remained transparent during polymerization. In contrast to this PU1900, 1600, 1000 and 750 have a melting point above 80 °C and turned turbid during polymerization. In these cases hard segments crystallized and are not available for side reactions anymore, although side reactions might occur at temperatures above the hard segment melting temperature. This is further supported by the observations that if PU2800 is synthesized at 60 °C (below the melting point) a polydispersity of 2.0 is found and if PU1600 is synthesized at 100 °C a polydispersity of 3.6 is obtained. An extra indication of this hypothesis is that PU2800 synthesized at 80 °C shows a multimodal molecular weight distribution while PU2800-60 °C shows a monomodal distribution. These results suggest that relative more side reactions occur at temperatures above the hard segment melting temperature, where the hard segments remain available for reaction.

3.2. Thermal properties

For high hard segment contents, the majority of hard segment is crystalline, while a decrease in amount of hard segment leads to a decrease in the percentage of crystalline hard segment. A decrease of T_g of PCL before chain extension is found with shorter chain length due to the increased concentration of end groups (Table 3). After chain extension an increase in T_g of the segments is found with decreasing PCL length, exactly the opposite. Generally, this increase in T_g is attributed to a certain degree of phase mixing of hard and soft segments. However, we found that with decreasing PCL length the degree of phase separation increases which would also decrease the influence of hard segment on the soft segment T_g . It is known from literature that (physical) crosslinks can have a major influence on the soft segment T_g [28]. According to the empirical formula from Nielsen a molar mass between crosslinks of 1000 g/mol (as estimation for PU750) can lead to an increase in T_g of 38 °C, while the measured difference is 34 °C [29]. This suggests that in this case the physical crosslinks have a larger influence on the soft segment T_g than phase mixing.

The PCL crystallinity of the polyurethanes were calculated using a heat of fusion of 136 J/g for 100% crystalline PCL (Table 3) taking into account the weight fraction of PCL in the PUs [30]. Under the

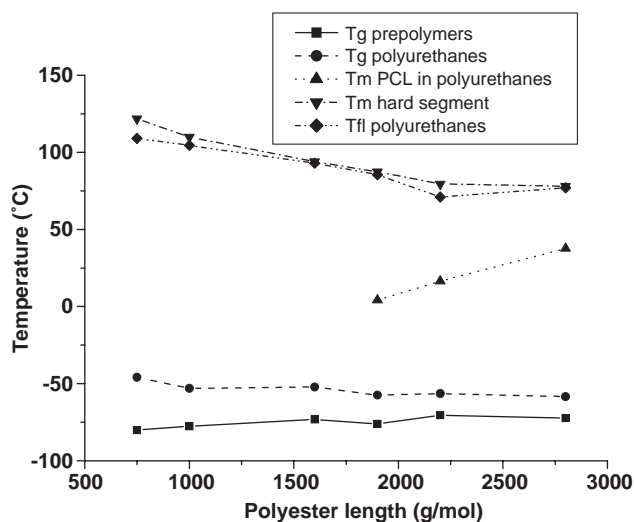


Fig. 5. Thermal transitions of the polyurethanes and the corresponding polyesters plotted as a function of the molecular weight of the polyesters.

circumstances used here no crystalline PCL was found for PU1600, PU1000 and PU750 while for PU1900, PU2200 and PU2800 a PCL melting point was found in the DSC thermograms. For the PUs an increase in polyester length results in a decreased crosslink density and an increased ability for chain folding.

The DSC thermograms of the polyurethanes also show a hard segment melting point. As can be seen in Fig. 5 and Table 3 there is an increase in melting point with an increase in hard segment content. The values for T_m found with DSC show a good correlation with the values for T_f determined with DMTA measurements.

For segmented copolymers, the decrease of hard segment melting point upon copolymerization with a soft segment can be explained with the solvent effect proposed by Flory [31,32]

$$\frac{1}{T_m} - \frac{1}{T_m^*} = -\left(\frac{R}{\Delta H_u}\right) \ln X_A. \quad (2)$$

Here T_m is the observed copolymer melting temperature and T_m^* is the observed melting temperature of the homopolymer A. X_A is the mole fraction of A-units in the copolymer, ΔH_u is the latent heat of melting of A-units of homopolymer A and R is the gas constant. Although the theory is originally based on random copolymers it has also been applied for segmented copolymers [33,34].

According to this theory of Flory, the molar volumes of the crystallizable and non-crystallizable monomeric units should be equal. We estimated the molar volumes off both the hard segment unit and the ϵ -caprolactone repeating unit according to the group contribution method of Van Krevelen [28]. According to this method it is of some importance whether these groups are considered to be crystalline or amorphous. If the hard

segment is assumed 100% crystalline the molar volume of the hard segment is 2.67 times larger than the molar volume of one repeating unit ϵ -caprolactone (the central BDO initiator unit is considered to be equal to ϵ -caprolactone). For the amorphous assumption the factor is 2.98. Both values were used in the following formula:

$$X_A = \frac{C}{C + (M_n/114.14)}. \quad (3)$$

Here C is the molar volume correction factor of either 2.67 or 2.98 and M_n the molecular weight of the poly(ϵ -caprolactone) soft segment and 114.14 g/mol is the molecular weight of one ϵ -caprolactone unit.

If Eq. (2) is rewritten to Eq. (4) a linear fit can be obtained as is shown in Fig. 6.

$$\frac{1}{T_m} = a[-\ln(X_A)] + b, \quad (4)$$

where a and b are the slope and intercept, respectively.

Eq. (4) can also be used to calculate the melting point of pure hard segment by extrapolating to $X_A = 1$. This gives a value of 190 °C, using the crystalline hard segment value. In order to verify this value a comparison was made with the synthesized model compound with a hard segment content of 80.8 wt%. With DSC the melting point of this component was measured as 166 °C. The calculated melting temperature for 80.8 wt% hard segment in the polymer is 169 ± 9 or 166 ± 9 °C for the crystalline and amorphous hard segment assumption, respectively. The measured melting point is in very close agreement with these calculated values.

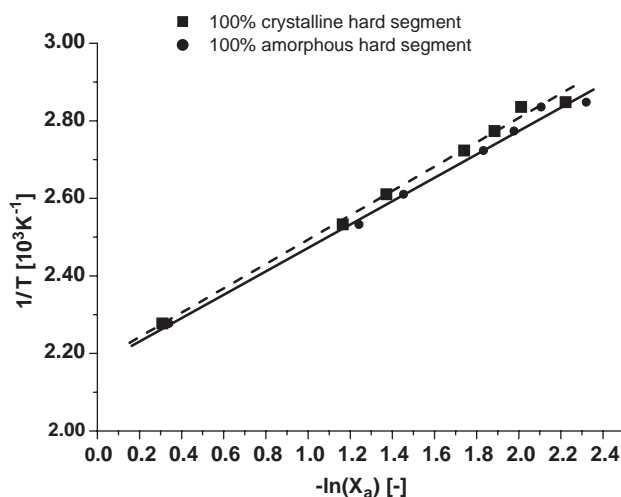


Fig. 6. Reciprocal of the melting temperature as a function of the mole fraction of hard segment. The dotted line is determined assuming 100% crystalline hard segment while the solid line is obtained assuming 100% amorphous hard segment.

Table 4

Measured and calculated ΔH and the accompanying percentage of crystalline hard segment

Polyurethane	Hard segment content (–)	ΔH_{meas} (J/g)	$\Delta H_{\text{calc,CA}}$ (J/g)	$\Delta H_{\text{calc,AA}}$ (J/g)	CHS _{CA} (%)	CHS _{AA} (%)
PU750	0.33	51.7	64.4	70.6	80	73
PU1000	0.27	38.4	52.7	57.8	73	66
PU1600	0.19	22.3	36.6	40.2	61	55
PU1900	0.16	15.4	31.8	34.9	48	44
PU2200	0.14	15.0	28.1	30.8	54	49
PU2800	0.12	5.2	22.8	25.0	23	21

AA: amorphous hard segment assumption, CA: crystalline hard segment assumption, CHS: hard segment crystallinity.

The solvent effect theory of Flory also makes use of ΔH_u . The slope of the curve fit of the hard segment melting points is used to calculate ΔH_{HS} . ΔH_u obtained from Eq. (2) is per mole unit, in this case mole soft segment. In order to convert this to the value per mole hard segment the molar volume correction factor of 2.67 and 2.98 are needed again. Values of 195 ± 13 or 214 ± 13 J/g are found for the crystalline and amorphous hard segment assumption, respectively. The measured value for the melting enthalpy of the hard segment model compound is 137 J/g which after correction for the 1-butanol ends yields 170 J/g for pure hard segment. The difference with the calculated values suggests that the model compound hard segment is only partially crystalline.

Using the calculated ΔH_u and the ΔH values obtained via DSC and Eqs. (5) and (6) one can determine the crystallinity of the different PU x 's (Eq. (5)).

$$\Delta H_{\text{theor}} = \Delta H_u \text{HSC} \quad (5)$$

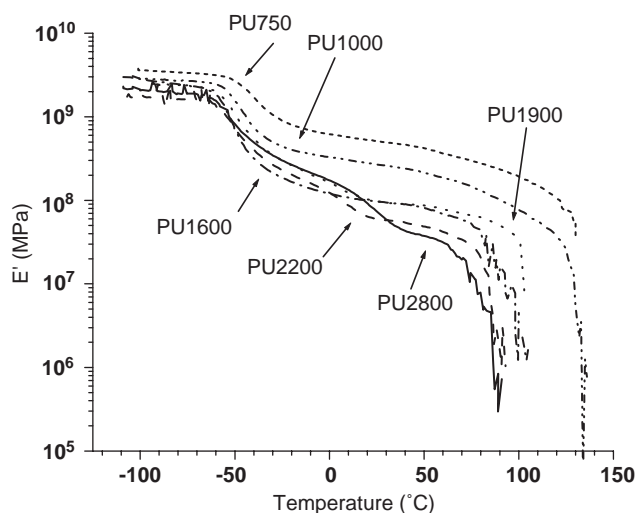
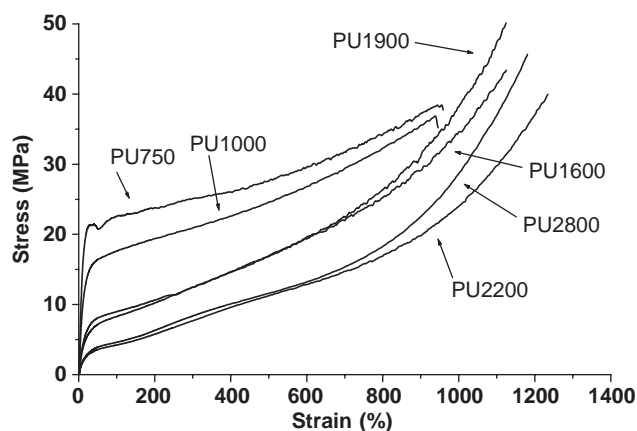
$$\text{Crystallinity} = \frac{\Delta H_{\text{measured}}}{\Delta H_u} 100\% \quad (6)$$

with HSC as hard segment content. The measured and calculated ΔH as well as the amount of crystalline hard segment can be found in Table 4.

3.3. Mechanical properties

3.3.1. DMTA

For the polyurethanes synthesized a decrease in soft segment length automatically leads to an increase in hard segment content. In Fig. 7 the storage modulus is shown versus temperature. The glass transition and the flow point are very clearly visible for all the polymers. The T_g originates from the soft segment phase, while T_f corresponds to the T_m of the hard segment. Polymers PU1900, PU2200 and PU2800 containing long soft segment show an additional transition around room temperature due to the presence of crystalline PCL. The hard segment crystallinity is a very important factor for the value of the storage modulus; higher hard segment crystallinity yields a higher rubber plateau.

Fig. 7. Storage modulus (E') versus temperature for PU x polyurethanes.Fig. 8. Stress strain curves of PU x copolymers at room temperature.

3.3.2. Tensile properties

The stress-strain curves of the different polymers are shown in Fig. 8. Characteristic values derived from these curves are presented in Table 5. Clearly three different regimes are visible. First, the behavior at low deformations can be explained as the pure elastic deformation belonging to regular elastomers [35]. With a decrease in

Table 5
Mechanical properties of PU_x polymers

Polymer code	Young's modulus (MPa)	Strain at break (%)	Tensile strength (MPa)	Tear energy (kJ/m ²)	Yield stress (MPa)	Yield strain (%)	Toughness (MPa)
PU750	263.9	870	38.7	236.6	16.2	10.1	251.3
PU1000	149.0	994	37.8	210.2	10.3	11.2	245.3
PU1600	64.6	1081	43.6	136.9	6.4	19.2	229.2
PU1900	54.6	1173	55.0	138.5	5.5	27.1	215.9
PU2200	30.1	1150	38.4	97.1	4.8	29.6	169.8
PU2800	33.8	1196	47.8	105.7	4.7	58.1	201.8

hard segment content the Young's modulus also decreases.

Secondly, the area of plastic flow. This is much the same for all the polymers studied, indicating a great possibility of shear induced crystal fragmentation. Thirdly, at strains above 600% an upswing in some of the curves can be observed, which can be attributed to strain induced crystallization of soft segment chains. For the shorter PCL segments this is not seen. Apparently, these chains are too short to crystallize even under applied strain.

Table 5 shows the dependence of the permanent deformation stress and strain on the hard segment content. An increase in hard segment content leads to an increase in yield stress, while an increase in hard segment content also leads to a decrease in strain at the yield point. The accompanying stress depends on crystallinity and lamellar thickness [36,37]. Uniform hard segments are used and consequently only the hard segment crystallinity, PCL crystallinity and PCL lamellar thickness influence the permanent deformation stress. If no crystalline PCL is present the stress is only dependent on the percentage crystalline hard segment since the thickness of the hard segment crystalline lamellae is constant. For the lower hard segment contents, however, there is no further decrease with a decrease in hard segment content, the presence of some crystalline PCL gives a deviation to higher values for the stress at permanent deformation.

For the strain at break and in a lesser extent also for the stress at break, an increase is found for the lower hard segment content polyurethanes. Most likely this is due to the difference in molecular weight of these polymers and not due to the difference in hard segment content. This is demonstrated in Fig. 9, where PU1000 samples with two different intrinsic viscosities are compared. An increase in intrinsic viscosity leads to an increase in both strain and stress at break [37].

3.3.3. Tear strength

In the past a lack of tear strength made it impossible to suture meniscus scaffold without tearing it [17,38]. Fig. 10 shows the dependence of tear strength as a function of hard segment content. As can be seen a

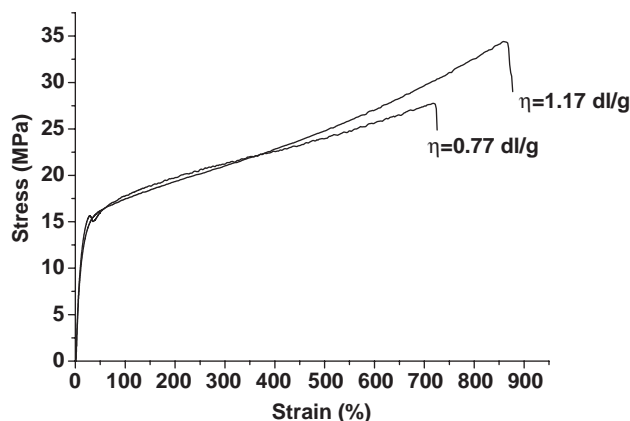


Fig. 9. Stress-strain curves for two PU1000 batches with a difference in intrinsic viscosity.

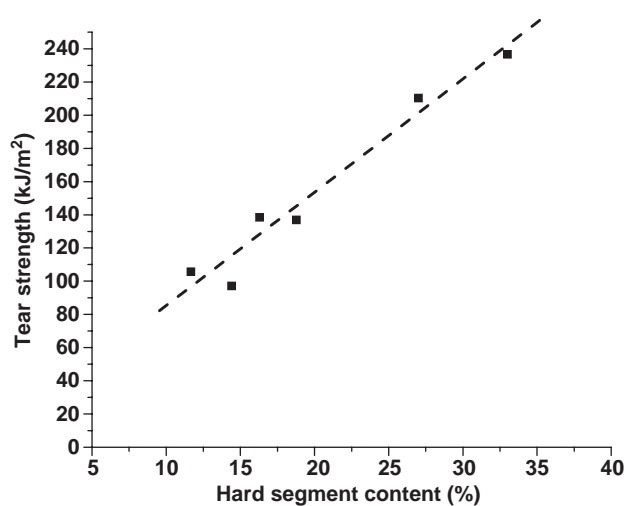


Fig. 10. Tear strength of PU_x based copolymers.

linear relationship between the tear strength and the hard segment content is found. As mentioned before the lower hard segment content polymers also show some crystalline PCL while this does not seem to influence the tear strength.

It should also be noted that the amount of crystalline hard segment is the major factor that determines the resistance to tear and not the built in hard segment

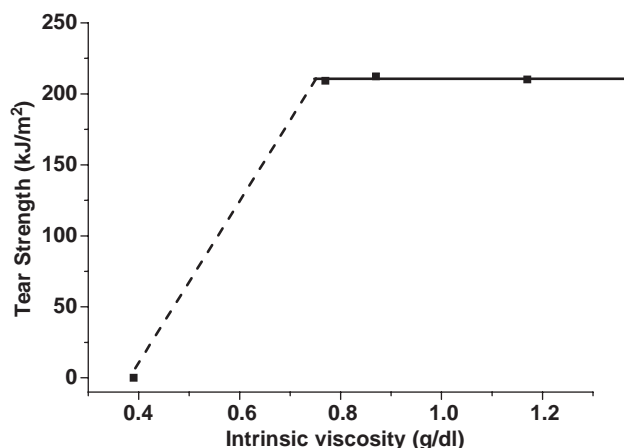


Fig. 11. Tear strength for four PU1000 batches with different intrinsic viscosities.

content. Due to the linear relationship between the hard segment content and the hard segment crystallinity (or the melting enthalpy) there is also a linear relation between the hard segment content and the tear strength. In principle two polymers with different hard segment content, but with the same hard segment melting enthalpy will have the same tear strength.

The influence of the molecular weight of the polyurethane on the tear strength is also a very important. Since the polymer is meant to degrade, with time, the molecular weight of the polyurethane will decrease. During this period the tear strength should remain high enough. As can be seen in Fig. 11 the polymer maintains constant tear strength as long as the molecular weight, here expressed as intrinsic viscosity, remains above a minimum value. If the molecular weight drops below this critical value the tear strength is lost completely even though this material is still phase separated and has a hard segment melting point.

4. Conclusions

High molecular weight segmented polyurethanes were synthesized without the use of solvents or catalysts. Chain extension below the hard segment melting point results in a polydispersity of two while chain extension above the melting point lead to broader polydispersities.

Polyurethanes based on PCL lengths of 1600 g/mol and shorter contain a crystalline urethane and an amorphous PCL phase with some dissolved hard segments. Polyurethanes with PCL segments longer than 1600 g/mol show an additional crystalline PCL phase. No indication for a separate amorphous hard segment phase was found.

Depending on hard segment content the values for the Young's modulus varied between 30 and 264 MPa and

the strain at break varied between 870% and 1196%. The tear strength varied between 97 and 236 kJ/m².

The polymers described here are also biologically evaluated and processed into meniscus reconstruction scaffolds [39,40].

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